A New Synthesis of *cis*-9,10-Epoxyoctadecane

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Received July 3, 1958

Boeseken and Belinfante[2] in a four step synthesis prepared *cis*-9,10-epoxyoctadecane by epoxidation of *cis*-9,10-octadecene which they obtained by the reduction of oleyl iodide with a copper-zinc couple in acetic acid.

We have prepared *cis*-9,10-epoxyoctadecane by a new three step synthesis. Oleyl alcohol was converted to oleyl tosylate, and the latter was cleaved with $LiAlH_4$ to *cis*-9,10-octadecene which was then epoxidized with peracetic acid to give the desired compound in 47% over-all yield.

The geometrical structure of the *cis*-9,10-epoxyoctadecane was verified by the appearance in its infrared absorption spectrum of a peak at 825 cm.$^{-1}$ which Shreve *et al.*[3] reported to be characteristic of *cis* epoxides, and by the absence of a peak at 893 cm.$^{-1}$ which they reported to be characteristic of *trans* epoxides. A peak was also observed at 905 cm.$^{-1}$ which was shown to be present in *cis*-9,10-epoxyoctadecanol and absent in *trans*-9,10-epoxyoctadecanol. This new peak was obscured in previous work with the isomeric epoxystearic acids and esters[3] by the COO vibrations in this region.

Table I lists the physical properties of *cis*-9,10-epoxyoctadecane and its intermediates.

EXPERIMENTAL

Oleyl alcohol. Commercial oleyl alcohol, Cachalot 0-8 grade, obtained from M. Michel and Co.[4] was purified by the method of Swern, *et al.*[5] The cuts boiling between 184–187° at 4.5 mm., n_D^{25} 1.4590, iodine value 93.5 (purity 98.6%) were used to make the tosylate. Infrared analysis showed this material to contain about 2% elaidyl alcohol.[3]

Synthesis of oleyl tosylate. The procedure of Shirley[6] was followed essentially, except that the *p*-toluenesulfonyl chloride was added as a pyridine solution. After the reaction mixture had been stirred at 10 ± 2° for 6 hr., it was poured into cold water and transferred to a separatory funnel. The upper oil layer was washed with two successive portions of cold methanol. The lower (tosylate) layer from these extractions was drained into a round-bottom flask, and the pyridine and methanol were removed *in vacuo* under a stream of nitrogen. The resulting tosylate (iodine value 54–57) was poured into three times its volume of diethyl ether and was refrigerated overnight. A white precipitate (m.p. 115–117°, 2.67% N, 7.01% S, water soluble), possibly the octadecenyl pyridinium complex of *p*-toluenesulfonic acid, was filtered out. (The presence of pyridine hinders the precipitation.) When the ether was removed, the yield of oleyl tosylate was 65%. Iodine value 59.7 (calcd. 60.2), n_D^{25} 1.4904.

Anal. Calcd. for $C_{25}H_{42}O_3S$: C, 71.04; H, 10.02; S, 7.59. Found: C, 68.21; H, 9.22; S, 7.15.

Cleavage of oleyl tosylate. A solution of 8.4 g. (0.02 mole) of oleyl tosylate dissolved in 60 ml. of distilled tetrahydrofuran (dried over sodium) was added in 1 hr. to a vigorously stirred, refluxing mixture of 1.2 g. of $LiAlH_4$ in 100 ml. of tetrahydrofuran. Agitation and refluxing were continued for a total of 10 hr. At the end of 5 and 7 hr., respectively, additional 0.3-g. portions of $LiAlH_4$ were added. This maneuver improved the yield of octadecene considerably. During the reflux period the refractive index of the oil (after the solvent from a 5 ml. sample had been evaporated) was observed to drop from 1.4904 to 1.4455 at 25°. Longer refluxing did not lower the refractive index.

Excess $LiAlH_4$ was decomposed in the usual manner with ethyl acetate, metallic complexes were decomposed with dilute HCl, and the organic layer was extracted with ether and separated. The ethereal layer was washed with cold water until acid free, dried over $CaSO_4$, and the solvents distilled off. The crude yield of *cis*-9,10-octadecene was 5.0 g. (100%).

Some purification was achieved by adsorption of the crude oil on a column of activated alumina and elution with diethyl ether. On removal of the ether from the eluate, 4.6 g. (92% recovery) of colorless oil was obtained which had an iodine value of 96.5 (calcd. 100.8), n_D^{25} 1.4452. A second alumina treatment raised the iodine value to 98.5 and lowered the refractive index to 1.4448 without loss in yield.

Anal. Calcd. for $C_{18}H_{36}$: C, 85.63; H, 14.37. Found: C, 85.81; H, 13.96.

On a larger scale, 168.8 g. (0.4 mole) of oleyl tosylate were reduced by the same method and purified by distillation to give an 85% yield of 98.6% pure *cis*-9,10-octadecene, n_D^{35} 1.4410, b.p. 109°/0.1 mm., iodine value 99.0.

Epoxidation to cis-9,10-epoxyoctadecane. The procedure of

(1) Fellow of National Renderers Association.

(2) J. Boeseken and A. H. Belinfante, *Rec. trav. chim.*, **45**, 914 (1926).

(3) O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, *Anal. Chem.*, **23**, 277 (1951).

(4) Reference to commercial products does not imply endorsement by the United States Department of Agriculture over similar products not mentioned.

(5) D. Swern, H. B. Knight, and T. W. Findley, *Oil & Soap*, Vol. **XXI**, 133 (1944).

(6) D. A. Shirley and W. H. Reedy, *J. Am. Chem. Soc.*, **73**, 458 (1951).

(7) B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, 3156 (1953).

TABLE I

PROPERTIES OF *cis*-9,10-EPOXYOCTADECANE AND ITS INTERMEDIATES

Compound	B.P., °C./Mm.	M.P.,[a] °C.	F.P.,[a] °C.	Iodine Values		n_D^{25}	n_D^{35}
				Calcd.	Found		
Oleyl alcohol[b]	184–187/4.5	—	—	94.8	93.5	1.4590	—
Oleyl tosylate	—	—	−30	60.2	59.7	1.4904	1.4866
cis-9,10-Octadecene	109/0.1	—	−35[c]	100.8	99.0	1.4448[c]	1.4410
cis-9,10-Epoxyoctadecane	—	22–23[d]	22	0.0	0.8[e]	1.4432	1.4395

[a] Uncorrected. [b] Contains 2% *trans* by infrared absorption[3] and 1–4% saturates (from iodine values). [c] Reported by Elsner and Paul[7] to be −30.5° and 1.4450, respectively. Reported by Boeseken and Belinfante[2] to be −15° and 1.4483 at 20°, respectively. [d] Reported by Boeseken and Belinfante[2] to be 0°. [e] Trace of *trans* olefin (determined by infrared analysis).

Findley, Swern, and Scanlan[8] for the epoxidation of unsaturated fatty materials with peracetic acid was employed. The yield of *cis*-9,10-epoxyoctadecane was 82%, m.p. (uncorr.) 22–23°, n_D^{25} 1.4395.

Anal. Calcd. for $C_{18}H_{36}O$: C, 80.52; H, 13.52; Oxirane O, 5.96. Found: C, 80.43; H, 13.22; Oxirane O,[9] 5.86.

(8) T. W Findley, D. Swern, and J. T. Scanlan, *J. Am. Chem. Soc.*, **67**, 412 (1945).

(9) A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

Acknowledgment. We wish to thank C. R. Eddy and his staff at the Eastern Utilization Research and Development Division for the infrared analyses.

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